Editors' Suggestion

Phase Separation in Cold Para-H_2 D_2 Clusters

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(Received 26 January 2024; accepted 11 April 2024; published 15 May 2024)

Low temperature phase separation in mixtures of ^{3}He and ^{4}He isotopes is a unique property of quantum fluids. Hydrogen has long been considered as another potential quantum liquid and has been predicted to be superfluid at $T \leq 1$ K, well below freezing temperature of ≈ 14 K. Phase separation has also been predicted in mixtures of *para*-H_2 and D_2 at temperatures ≤ 3 K. To defer the freezing, we produced clusters containing *para*-H_2 and D_2 at an estimated temperature of ≈ 2 K whose state was studied by vibrational Raman spectroscopy. The results indicate that the clusters are liquid and show the phase separation of the isotopes. The phase separation is further corroborated by the quantum molecular dynamics simulation.

DOI: 10.1103/PhysRevLett.132.206001

Phase separation at low temperature is a unique property of quantum fluids. It is well known that mixtures of helium isotopes ^{3}He and ^{4}He phase separate into superfluid and normal fluid phases at temperatures below 0.87 K [1]. Hydrogen has long been considered as another potential quantum liquid and has been predicted to be superfluid at $T \approx 1$ K in the bulk [2–4] and ≈ 2 K in small clusters [5–8]. Phase separation has also been predicted in mixtures of p-H_2 and D_2 at temperatures ≤ 3 K [9–12], where it derives from different zero point energies in neat and mixed substances. Solidification of hydrogen at $T < 13.8$ K presents the major obstacle for observation of the quantum liquid properties. Considerable attempts at supercooling liquid hydrogen have proven unsuccessful [13–15]. Concurrently, no evidence has ever been seen in the liquid phases of H_2/D_2 for anything but complete miscibility [16]. Mixtures of H_2 and D_2 have freezing points in the range of 14–19 K, depending on the D_2 content. Observation of phase separation in a solid is complicated by the low rate of diffusion. Study of the phase separation in clusters is enticing because the freezing temperature is usually depressed in the clusters. Several computational studies predicted the phase separation in equilibrium small mixed H_2/D_2 clusters consisting of less than about 50 molecules [17–21]. Experimentally, the clusters could be produced and studied on the microsecond time scale which may also enable observation of the metastable liquid phases. We have shown that liquid para hydrogen (p-H_2) clusters at $T \approx 2$ K can be obtained in a cryogenic nozzle beam expansion [22,23]. In this Letter, we studied the state of the cold mixed p-H_2/D_2 clusters via vibrational Raman spectroscopy of p-H_2 molecules. Our results indicate phase separation into nearly pure p-H_2 and D_2 phases in the surface and interior of the cold liquid cluster, respectively. The occurrence of the phase separation in clusters is also supported by the quantum molecular dynamics (MD) calculation.

The molecular beam apparatus is described in detail elsewhere [24]. The clusters are formed by a pulsed cryogenic free jet expansion of either liquid hydrogen or gas mixture containing 1% of hydrogen in He at stagnation pressure and temperature of $P = 3$ atm, $T = 22$ K and $P = 20$ atm, $T = 15$ K, respectively. Prior to experiments, the desired p-$H_2/D_2/He$ mixtures were prepared in a high pressure sampling cylinder. p-H_2 was produced from liquid H_2 by catalytic conversion of *ortho*-$H_2(o - H_2)$ [25]. The vibrational spectra of the p-H_2 molecules in clusters were obtained via coherent anti-Stokes Raman spectroscopy-CARS [22] at distance from the nozzle of $L = 10$–35 mm. The laser system was calibrated using Raman spectrum of p-H_2 gas.

Previous CARS measurements [22] indicated that the clusters produced upon the cryogenic expansion of neat p-H_2 liquid are solid and have estimated temperature of about 10 K. In comparison the expansion of the mixture composed of 1% of p-H_2 in 99% of helium gas yielded liquid supercooled clusters containing about 10^4 molecules at estimated temperature of 1–2 K [22]. These two modes of expansion are used in this Letter to study the state of the mixed p-H_2/D_2 clusters. The measurements in solid clusters provide a useful reference as they likely contain a homogeneous mixture of p-H_2 and D_2 molecules, owing to high temperature as well as low rate of diffusion of the molecules in a solid. On the other hand, the clusters produced upon expansion of p-$H_2/D_2/He$ mixtures are colder and their liquid state facilitates diffusion required for the phase separation.

p-H_2 molecules have nuclear spin $I = 0$ and at low temperature reside in the ground rotational state $J = 0$, giving rise to a strong $Q_1(0)$ line ($\nu = 1$, $\mathrm{J} = 0 \leftarrow \nu = 0$,

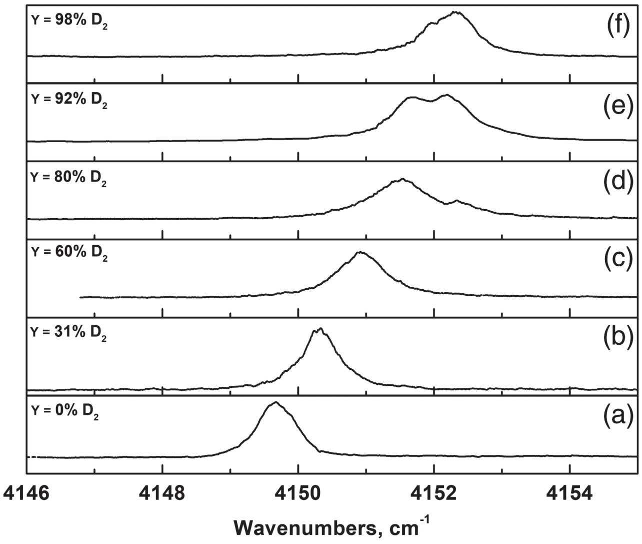

FIG. 1. CARS spectra in the vicinity of the $Q_1(0)$ line of p-H_2 in clusters obtained upon expansion of liquid p-H_2/D_2 mixture with varying D_2 content, Y. Spectra were obtained at $L = 10$ mm with instrumental resolution of 0.3 cm^{-1}.

J = 0). Figure 1 shows the CARS spectra in the vicinity of the $Q_1(0)$ line in clusters obtained upon expansion of the liquid p-H_2/D_2 mixture with different mole fraction of D_2, Y. Upon expansion, the liquid breaks into clusters which freeze before the observation point [22]. Figure 1 shows that upon increase of Y, the $Q_1(0)$ line shifts towards higher frequency. At $Y = 98\%$, in panel (f), the spectrum has a band at 4152.25 cm^{-1}, which is shifted by approximately 2.6 cm^{-1} towards high frequency from that in the trace (a) at $Y = 0\%$.

Figure 2 shows typical CARS spectra of the $Q_1(0)$ line in clusters obtained upon gas expansion of 1% mixture of p-H_2/D_2 in He. It is seen that upon the increase of Y the frequency of the $Q_1(0)$ transition increases, but the shift remains much smaller than that in Fig. 1.

Figure 3 shows the results of the measurements of the frequency of the $Q_1(0)$ line in clusters versus the D_2 content upon expansion of neat liquid p-H_2/D_2 and 1% p-H_2/D_2 gas mixture in He in panels (a) and (b), respectively. Solid and open shapes indicate frequencies obtained at a distance from the nozzle of $L = 10$ mm and larger distances as specified, respectively. It is seen that in clusters obtained upon expansion of neat liquid p-H_2/D_2 in panel (a), the frequency of the $Q_1(0)$ rises approximately linearly with Y. Similar frequencies obtained at different distance from the nozzle. The variation of the frequency is much smaller in Fig. 3(b) which was obtained upon expansion of the mixture diluted in He. At small D_2 content, the frequency of the line rises with Y although the slope of the dependence can be estimated to be a factor of 5 smaller than in Fig. 3(a). At higher $Y > 35\%$, the frequency of the line is approximately independent of Y. The spectra could not be obtained at $Y > 70\%$ as the intensity of the CARS signal diminishes upon further dilution. The measurements at larger distance from the nozzle of 15 mm (open symbols) show even weaker dependence of the frequency on the D_2 content.

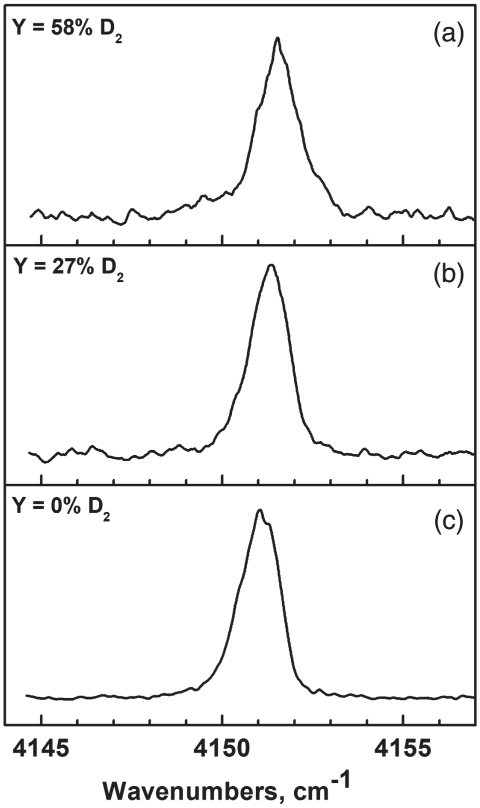

FIG. 2. CARS spectra of the $Q_1(0)$ line of p-H_2 molecules in clusters obtained upon expansion of gas having 1% p-H_2/D_2 in He and different values of Y as indicated in each panel. The spectra were measured at $L = 10$ mm with instrumental resolution of 0.3 cm^{-1}.

The physical origin of the vibrational frequency shift in condensed phase p-H_2 and its mixtures is well understood [26–31]. The frequency of the $Q_1(0)$ line in p-H_2 solid is about 11.4 cm^{-1} lower than that in the gas phase [32] at 4161.1687 cm^{-1}. 8.7 cm^{-1} of the shift is accounted for by isotropic dispersion intermolecular interactions [30]. In addition, the vibrational excitation is delocalized between p-H_2 molecules in the solid giving rise to a 3.6 cm^{-1} wide vibron band [29,33]. Only Raman transitions to the lowest ($k = 0$) level of the vibron band are allowed, thereby producing a very sharp $Q_1(0)$ line. [29] As a result, the frequency of the $Q_1(0)$ line in p-H_2 solid has an additional 2.7 cm^{-1} downward shift [30]. Similar effects cause the vibrational shift in liquid p-H_2 [34]. Our Raman spectroscopic study [35] of condensed p-H_2 at different temperature shows that the frequency shift of the $Q_1(0)$ line in liquid and in solid can be fitted by the same function of density, confirming similar origin of the line shift in solid and in liquid.

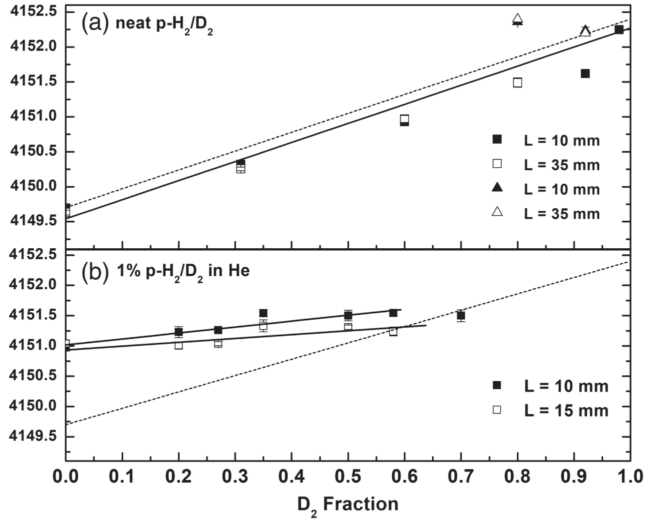

FIG. 3. Frequencies of the $Q_1(0)$ line in p-H_2/D_2 clusters versus D_2 content, Y, upon expansion of neat p-H_2/D_2 liquid and 1% p-H_2/D_2 in He gas in panels (a) and (b), respectively. Triangles in panel (a) represent the higher frequency components of the $Q_1(0)$ line as observed in panels (d) and (e) of Fig. 1. Each point represents the frequency average obtained from three to five spectra. The scattering of the measurements is typically smaller than the size of the symbols. The solid lines are linear fits. The dashed line represents the frequency dependence expected in bulk solid mixtures.

The frequency of the $Q_1(0)$ line is a sensitive probe for the composition of the condensed hydrogen. In p-H_2-D_2 mixtures, the probability of the vibron hopping decreases leading to the narrowing of the vibron band and concomitant upward shift of the frequency of the $Q_1(0)$ line. Although the spectra of the $Q_1(0)$ line of p-H_2 in p-H_2/D_2 have not been examined, its frequency could be anticipated based on the previous studies in other mixtures. In solid samples of mixed p-H_2/o-H_2, the frequency of the $Q_1(0)$ line shifts linearly with o-H_2 content [30]. Similarly in D_2/H_2 and D_2/HD solids, the frequency of the $Q_1(0)$ of D_2 increases linearly with $H_2(HD)$ content [31]. Furthermore, the shift of the $Q_1(0)$ line of D_2 was found to be the same in D_2/HD and D_2/H_2 mixtures of the same D_2 content. Dashed lines in Fig. 3 show the expected dependence of the frequency of the $Q_1(0)$ line of p-H_2 vs the fraction of D_2 molecules in the solid, which must be the same as measured in the p-H_2/o-H_2 solid vs fraction of the o-H_2 molecules [30].

Clusters obtained upon expansion of neat p-H_2/D_2 liquid, see Fig. 3(a), provide the closest comparison to the bulk material. The frequency of the $Q_1(0)$ line in clusters at 4149.7 cm^{-1} obtained in neat p-H_2 clusters matches that in bulk solid [28,35]. The addition of D_2 induces a high frequency shift which scales linearly with Y. Good agreement of the measured and predicted dependence of the $Q_1(0)$ frequency vs Y indicates that the clusters have the same p-H_2 vs D_2 composition as in the expanding liquid and do not show any phase separation.

We proceed with a discussion of the results obtained upon gas expansion of p-H_2/D_2 diluted in helium as summarized in Fig. 3(b). Previous rotational CARS measurements indicated that p-H_2 clusters obtained at similar conditions consist of about 10^4 molecules and are liquid [22]. Figure 3(b) shows that at $L = 10$ mm and increasing D_2 content, Y, the frequency of the $Q_1(0)$ line first rises by about 0.4 cm^{-1} at $Y = 35\%$ and then remains constant at about 4151.52 ± 0.02 cm^{-1} at larger Y. At larger $L = 15$ mm, the frequency is about 4151.29 ± 0.05 cm^{-1}, only slightly higher than the frequency in neat p-H_2 clusters at 4151.01 ± 0.05 cm^{-1}. The saturation of the frequency dependence at $Y \geq 35\%$, implies that further increase of the D_2 content in clusters does not lead to a reduction of the number of nearest neighbor p-H_2 molecules in the vicinity of a given p-H_2 molecule. This behavior is consistent with the phase separation in the p-H_2/D_2 cluster. Smaller frequency change at larger distance from the nozzle indicates that the phase separation is more complete. The flight time of the clusters from the nozzle to the observation point at $L = 10$ mm is about 25 μs. Phase separation requires some time for molecules to diffuse through the cluster at low temperature, consistent with more complete separation at larger distances. The temperature of the clusters is also expected to decrease downstream, favoring more complete phase separation as will be discussed later. From the frequency shift, the fraction of the D_2 molecules in the H_2 rich phase can be estimated, as shown in Fig. 4.

In addition to the experiments, the phase separation in the mixed clusters composed of $320H_2$ and $320D_2$

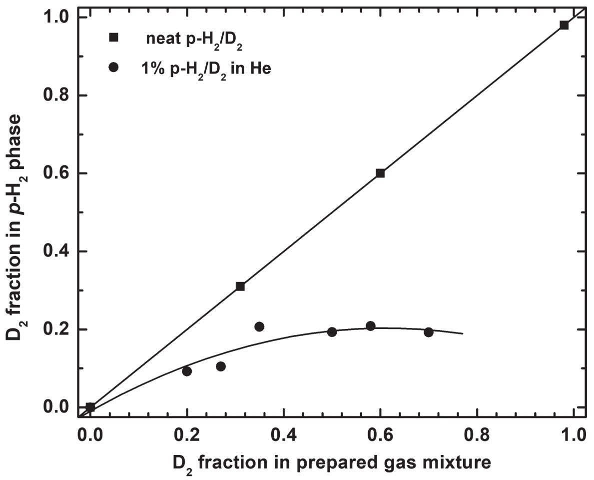

FIG. 4. Fraction of D_2 molecules in the p-H_2 rich phase of clusters vs content of D_2 in the prepared samples. Solid squares obtained upon expansion of neat liquid p-H_2/D_2 mixtures. Solid circles obtained upon expansion of diluted p-H_2/D_2 mixture as measured at $L = 10$ mm.

molecules, was studied by a real-time quantum MD calculation by the nuclear and electron wave packet molecular dynamics (NEWPMD) method which is further explained and discussed in Supplemental Material [36], which includes Refs. [37–42]. The NEWPMD technique was developed for a condensed phase containing H_2 and D_2 molecules to describe not only equilibrium but also non-equilibrium states. It takes into account the strong and differently pronounced quantum properties of H_2 and D_2 molecules such as nuclear delocalization and zero-point energy [37–42].

Figure 5 shows the time evolution of the radial distributions for the center of mass (c.m.) coordinates of H_2 and D_2 molecules in the mixed cluster of about 5 nm in diameter during the cooling process. The cluster that was initially equilibrated at 25 K shows almost uniform radial distributions of the H_2 and D_2 molecules in the time window of 0–10 ps in Fig. 5(a). The cooling was simulated by applying the Berendsen thermostat with a correlation time of 1 ps and temperature of 3 K to the outermost part of the cluster containing about 5% of the molecules. Figures 5(b) and 5(c) show that, during the cooling, H_2 molecules gradually move toward the surface region of the cluster while D_2 molecules gather around the cluster core, indicating the phase separation starting around 50 ps. The temperature of the cluster decreases from 25 K to almost 3 K within 50 ps, see Fig. S1 in Supplemental Material [36]) and the cluster enters the supercooled state, satisfying the estimated temperature condition for the H_2-D_2 phase separation [10–12].

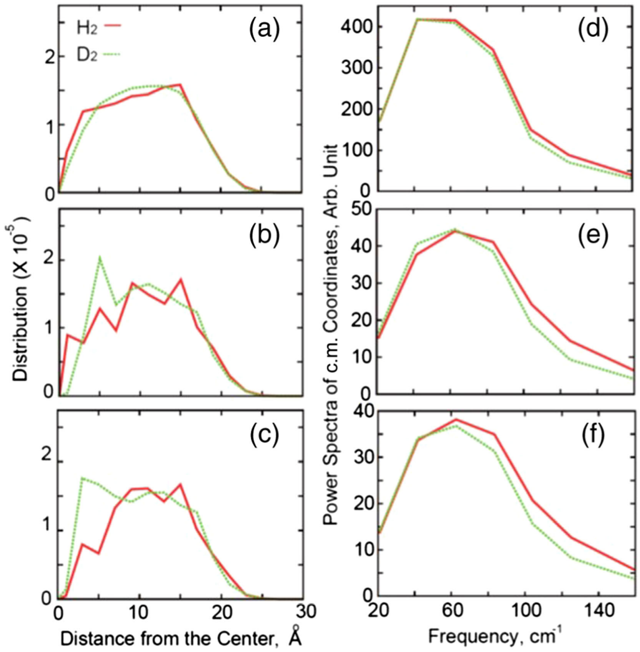

FIG. 5. (a)–(c) Radial distributions of H_2 molecules (red lines) and D_2 molecules (green lines) in the H_2-D_2 cluster during the cooling. The radial distance was defined as distance from the center of the H_2-D_2 cluster. Panels (a),(b), and (c) correspond to averaging over the time windows of 0–9.9, 30–39.9, and 40–49.9 ps, respectively. The three panels on the right show the corresponding power spectra of the c.m. coordinates. The results for H_2 and D_2 molecules are shown by red and green lines, respectively.

It is noticeable that the mixed cluster is not crystalized although it reaches the temperature of about 3 K, well below the H_2 freezing temperature in the bulk of about 14 K. Figures 5(d)–5(f) shows power spectra, which were obtained by Fourier transformations of the time-dependent c.m. coordinates of H_2 and D_2 molecules, to characterize the collective translational dynamics of the H_2 and D_2 molecules in the cluster during the cooling. At short time in Fig. 5(d), the H_2 and D_2 molecules have very similar power spectra. The obtained power spectra are typical for a supercooled liquid [40,42]. We note that the power spectrum obtained for solid H_2 at 2.5 K in a NEWPMD calculation using a unit cell composed of 640 molecules is qualitatively different from the current power spectra: Only in the case of the solid H_2, the sharp and distinct peak corresponding to the lattice E_{2g} mode appears [39]. Such qualitative difference indicates that the cluster is in a liquid state at temperature of 3 K well below the freezing temperature of hydrogen at ~14 K [40,42].

Because of smaller mass and concomitant larger zero-point energy and larger delocalization, the molar volumes for liquid and solid H_2 are larger than those for D_2 at the same temperature. Similarly, the binding energy of the D_2 molecules is larger than that for the D_2-H_2 or H_2-H_2 pairs. Therefore, at low enough temperature the D_2 molecules occupy the interior of the cluster, whereas the H_2 molecules reside on the surface. Although the same arguments are valid for the solid, the diffusion rate of the molecules in solid at low temperature is very slow, thus preventing any practical realization of the phase separation. In this Letter, we studied clusters which remain liquid within the time window in the experiment as well as in calculations. The time is sufficient for molecules to explore configurations close to the minimum free energy, which at low temperature corresponds to the phase separated cluster. Small size of the clusters studied in this Letter with large surface to volume ratio favors the realization of the phase separation. In a macroscopic sample of the mixed H_2-D_2, the surface to volume ratio becomes very small thus the time for diffusion of the H_2 molecules to the surface is much longer. On the other hand, the solidification is governed by the creation of the nucleation centers whose probability scales with the number of the molecules in the sample and becomes exponentially large in a macroscopic sample. Therefore, supercooling of the liquid hydrogen down to the temperatures of less or about 3 K relevant for the phase separation was never observed.

This Letter shows that small clusters are uniquely suited for the observation of the phase separation in H_2/D_2, which has long eluded experimental observation. The clusters are formed and cooled in a cryogenic nozzle beam expansion. The clusters remain liquid within about 20 μs of cooling time, which is sufficient for the liquid to separate into D_2 phase in the interior and H_2 phase on the surface. The quantum molecular dynamics simulation indicated that the phase separation stems from the differently pronounced quantum properties of the H_2 and D_2 molecules. This Letter shows the feasibility for preparation of the transient quantum fluids at a temperature well below the freezing point and opens the way for studying these molecular quantum fluids.

We are grateful to Melody Sun for her help with some of the experiments and data analysis described in this Letter as well as Melissa Gish for proofreading of the text. This material is based upon work supported by the NSF under Grants No. CHE-2102318 and No. DMR-2205081. K. H. D. thanks Kusunoki 125, PRESTO, Japan Science and Technology Agency Grant No. 22713147, Grant-in-Aids for Scientific Research from Japan Society for the Promotion of Science (KAKENHI) Grant No. 20K05419 and No. 18H05407, and Toyota Mobility Foundation.

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[36] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.132.206001 for the description of the NEWPMD method and Fig. S1 containing the snapshot of the center of mass positions of the H_2 and D_2 molecules in the cluster and the temperature of the molecules vs cooling time.

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